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Combining planar and central chirality in ferrocene thiophosphine-sulfoxides

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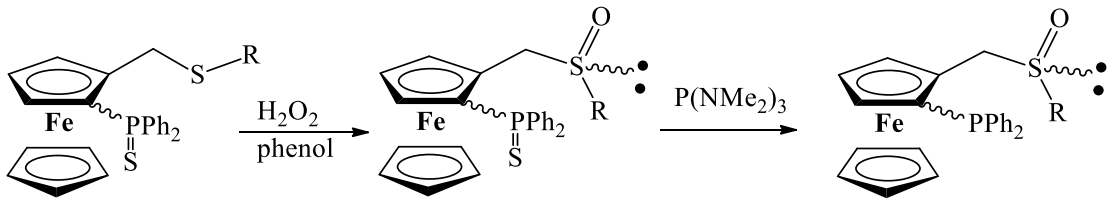
Abstract

New chiral ferrocenylthiophosphine-sulfoxide and phosphine-sulfoxidederivativespossessing planar chirality for theferrocenemoietyand central chirality at the sulfur atomhave been synthesized. These ligands could be obtained as pure diastereoisomersinboth racemic andenantiomerically pure forms. Complete characterization by XRD analysis has allowed the absolute configuration assignmentineachcase. Preliminarycoordination studies of the phosphine-sulfoxideligandson platinum are also reported. They show chelating complexationbythe phosphorous and sulfur atoms.

Image for the graphical abstracts:



R = Ph, Et, *t*Bu

1.Introduction

Various chiral bidentate ligands were developed over the past decades, possessing the chiral information on the carbon backbone or on the donor atom. Ligands with variouscombinations of donor atoms (in particular, P–P, P–N, or N–N ligands) have been extensively studied and a fewP-chirogenic compounds such as QuinoxP[1] or dipamp[2] are very effective in a variety of asymmetric catalytic processes. Recently, very efficient systems for asymmetric catalysis using P–S ligands with various backbones, havebeen reported.[3,4]Furthermore, several reports have described the preparation and the coordination chemistry of chiral phosphine sulfoxide ligands possessing the chirality on the sulfur atom, for example α-phosphinosulfoxides(PCSO[5]andPNSO[6]) or β-phosphinosulfoxides[7] (Figure 1). Riera and Verdaguer[8] described ligands with an extra chiral centerin the central carbon atom between P and SO and also camphor derivatives combininga chiral carbon backbone with sulfur chirality.[9]Kagan's methodology based on diastereoselective*ortho*-lithiation of ferrocenesulfoxide derivatives was used in order to synthesize phosphine-sulfoxide ligands with additional planar chirality.[10]We have recently developed syntheses of new chiral ferrocenylγ-P,S ligands in both racemic and enantiomerically pure form (R_{Fc} or S_{Fc}configuration), and reported on their coordination chemistry and applications to asymmetric catalysis, namely in asymmetric allylic substitution, alkene methoxycarbonylationand ketone hydrogenation.[11] Here we present the synthesis of new γ-ferrocenyl phosphine sulfoxide ligands (Figure 1)and preliminary studies on their coordination chemistry with platinum.

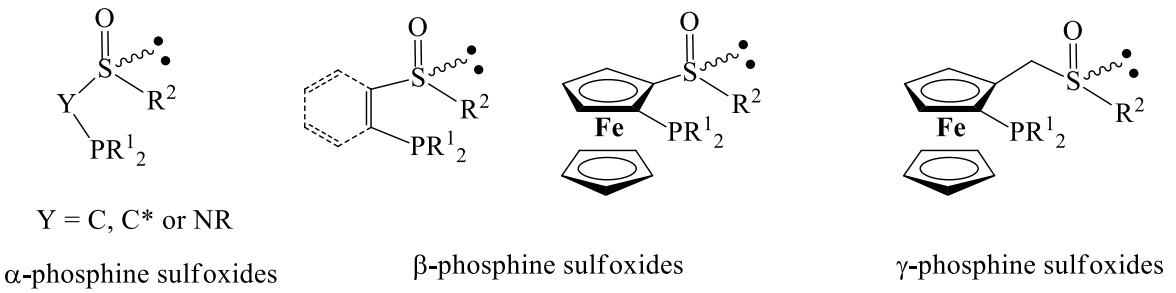


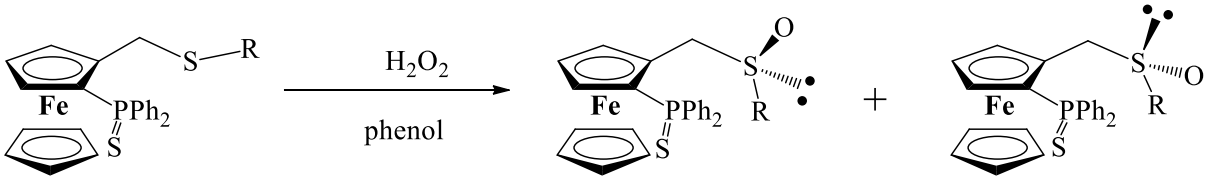
Figure 1α, β and γ phosphine sulfoxides

2. Results and Discussion

Starting from the chiral phosphine-thioetherligands already synthesized in our group, we have developed a new class of ferrocenyl phosphine-sulfoxides ligands based on the selective oxidation of the thioether functionality to sulfoxide. Thus, a central chirality on the sulfur atom (R_S or S_S) is added to the planar chirality of ferrocene (R_{Fc} or S_{Fc}).The two diastereoisomersthatcan*a priori*be formed must therefore be subsequently separated.

Afirst potential issue in the synthetic pathway to the thiophosphine-sulfoxides**2** fromthiophosphine-thioethers**1**(see scheme 1) is the possible over-oxidation to the corresponding sulfonesas well as oxidation of the iron atom to ferroceniumor conversion of

thethiophosphine to phosphine oxide, as already observed in the oxidation of related (2-diphenylthiophosphinoferrocenyl)methanol to the corresponding aldehyde.[12]Therefore, the mild method described by Liang Xu[13]using an aqueous solution of H_2O_2 in the presence of phenol was selected.Under these conditions, the racemic compounds **1a-c** (R = Ph, Et, *t*Bu) were transformed into the corresponding thiophosphine-sulfoxides**2a-c** with total conversion and chemoselectivity (no sulfoneor other by-products were observed). For each thioether, two diastereoisomers (each one as a pair of enantiomers)were obtained in a 1:1 ratio. These reactions are fast (2-3 minutes) andstrongly exothermic. For safety reasons, we therefore limited the thioetheramount (typically 250 mg) transformedineach run. Eachdiastereomercould be isolated in good yields after separation by column chromatography (Scheme 1).



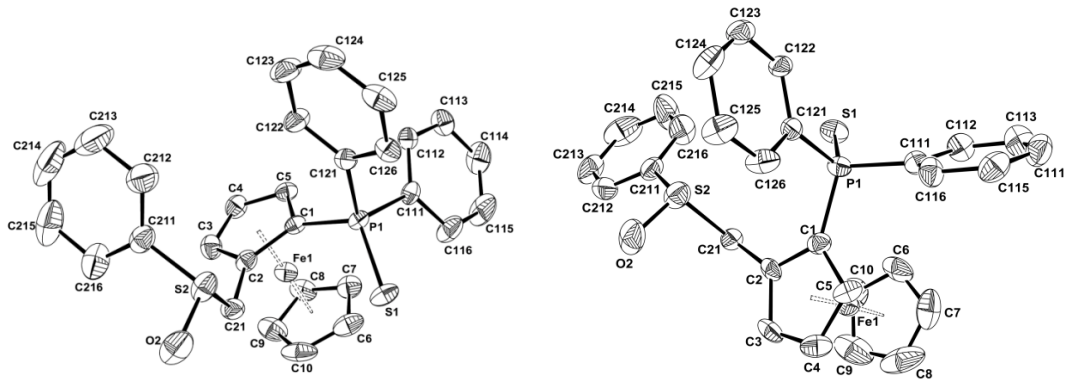
(*R*/*S*)$_{Fc}$-1a-c
1a (R=Ph)
1b (R=Et)
1c (R=*t*Bu)

(*R*/*S*)$_{Fc}$-2a-c

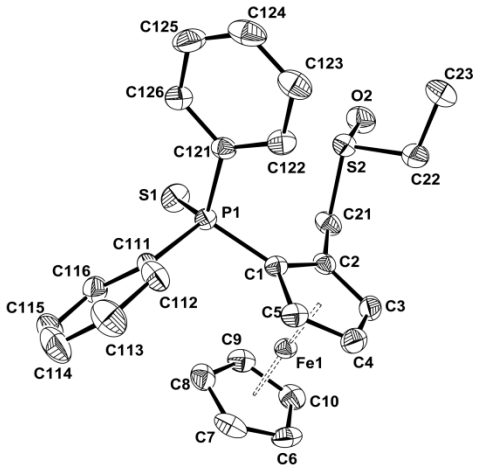
	dia1 + dia2	isolated dia1	isolated dia2
2a	91%	41%	44%
2b	93%	44%	42%
2c	92%	43%	40%

Scheme 1

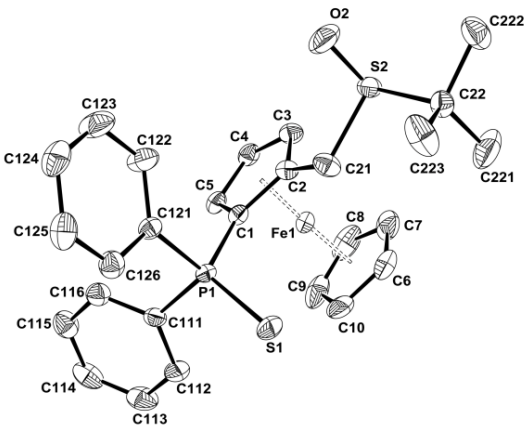
After diastereomerseparation, the sulfur atomconfigurations were established by single crystal X-ray diffraction analyses. Single crystals of **2a-Dia1**, **2a-Dia2**, **2b-Dia1**, **2c-Dia1** and **2c-Dia2**were obtained by slow diffusion of pentane vapors into a dichloromethane solution. Theseproductswere obtained from the racemic thiophosphine-thioethers**1a-c** (*R*/*S*$_{Fc}$) and crystallize as racemates, except for **2c-Dia2** which affords a twin by inversion, therefore also containing both enantiomers (70:30) in the crystal.

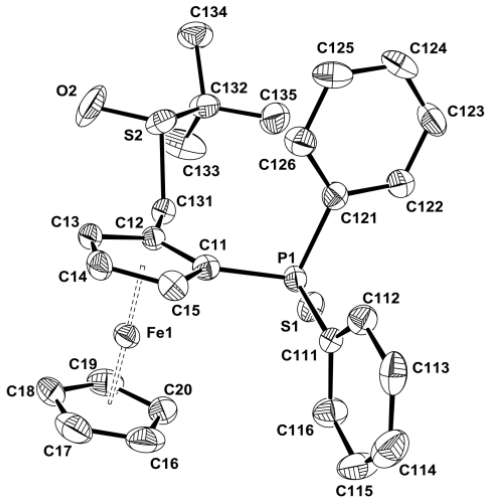


2a-Dia1 (R_{Fc}, S_S)/(*) **2a-Dia2** (S_{Fc}, S_S)/(*)



2b-Dia1 (R_{Fc}, R_S)/(*)





2c-Dia1 (S_{Fc}, R_S)/(*) **2c-Dia2** (S_{Fc}, S_S)/(*)

Figure 2.ORTEP views of**2a-Dia1**, **2a-Dia2**, **2b-Dia1**, **2c-Dia1** and **2c-Dia2** (* the other enantiomer is present in the crystal structure but not represented in the picture)with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for the sake of clarity.

To the best of our knowledge, these compounds are the first structurally characterized ferrocenylthiophosphine-sulfoxides.Selected geometrical parameters are reported in Table 1. The five compounds have similar structures with the protecting S(1)*endo* with respect to the Cp ring whereas the sulfido S(2) is *exo* (Table 1). The distances and angles within the sulfoxidemoietyare identical within experimental error. The two Cp rings are either nearly

eclipsed for **2a-Dia2**, **2c-Dia1**and **2c-Dia2B** and in between eclipsed-staggered for **2a-Dia1**,**2b-Dia1** and **2c-Dia2A** (τ values in Table 1).In compound **2c-Dia2**, there are two molecules within the asymmetric unit. These molecules have similar configuration as indicated by the molecular fitting shown in Figure 3. The only marked difference is the twist angles observed between the two Cp rings, 12.7(3)° for molecule A and 4.5(3)° for B.

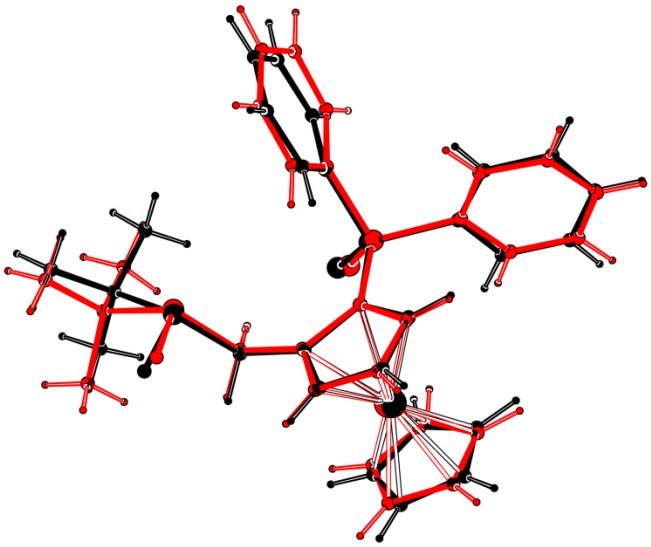


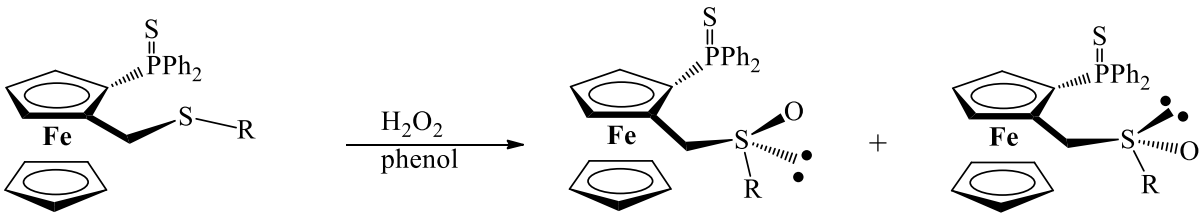
Figure 3. Molecular fitting of the two molecules **2c-Dia2A** and **2c-Dia2B.**

Table 1. Selected geometrical parameters for the structures of compounds **2**, **3** and **4**.

	2a-Dia1	**2a-Dia2**	**2b-Dia1**	**2c-Dia1**	**2c-Dia2A**	**2c-Dia2B**	**3a-Dia2**[a]	**4a**[b]
Distances (Å)								
Fe(1) - Cp(1)	1.6440(11)	1.642(4)	1.635(1)	1.640(1)	1.642(2)	1.644(2)	1.639(1)	1.646(2)
Fe(1) - Cp(2)	1.6582(14)	1.654(6)	1.652(2)	1.655(1)	1.655(2)	1.659(2)	1.653(1)	1.661(3)
C(1) - P(1)	1.788(2)	1.788(8)	1.802(3)	1.792(2)	1.788(4)	1.798(4)	1.816(2)	1.796(5)
P(1) - S(1)	1.9611(8)	1.958(3)	1.957(1)	1.9584(8)	1.958(2)	1.956(2)		
C(2) - C(21)	1.491(3)	1.502(11)	1.502(4)	1.500(3)	1.496(5)	1.495(5)	1.487(3)	1.481(8)
C(21) - S(2)	1.817(2)	1.828(8)	1.825(3)	1.811(3)	1.820(4)	1.817(4)	1.823(2)	1.810(5)
S(2) - O(2)	1.499(2)	1.485(6)	1.508(2)	1.494(2)	1.495(4)	1.480(4)	1.470(2)	1.459(3)
S(2) - C(22)	1.782(3)	1.787(9)	1.803(3)	1.841(3)	1.826(5)	1.840(4)	1.790(2)	1.782(6)
Angles (°)								
Cp(1) - Fe(1)-Cp(2)	178.53(7)	177.7(2)	177.29(8)	177.42(7)	178.5(1)	178.2(1)	177.90(5)	176.21(13)
C(2) – C(21) – S(2)	115.90(17)	111.0(5)	113.1(2)	110.5(2)	108.1(3)	107.5(3)	110.3(1)	116.2(3)
C(21) – S(2) – O(2)	103.28(13)	105.5(4)	105.5(1)	105.0(1)	103.8(2)	105.8(2)	105.6(1)	108.1(2)
C(21) – S(2) – C(22)	100.84(12)	94.4(4)	97.8(2)	101.0(1)	100.4(2)	100.6(2)	95.65(9)	97.5(2)
O(2) – S(2) – C(22)	107.50(13)	106.8(4)	106.9(2)	108.0(1)	108.0(2)	108.0(2)	107.5(1)	109.1(2)
Distances from plane (Å)								
S(1)---Cp(1)	-0.859(1)	-1.06(2)	-0.921(6)	-1.063(5)	-0.992(8)	-1.154(9)		
S(2)---Cp(1)	1.500(1)	1.63(1)	1.647(5)	0.457(5)	1.751(7)	1.757(7)	1.619(4)	0.970(9)
O(2)---Cp(1)	1.228(2)	2.49(1)	1.619(8)	1.945(5)	1.654(9)	1.895(8)	2.236(4)	2.186(9)
Twist angle for therCp rings (°).								
τ°	12.5(2)	4.0(9)	13.3(2)	1.6(3)	12.7(3)	4.5(3)	4.7(2)	14.5(3)

[a]: **3a dia2: (S_{Fc}, S_S)/(R_{Fc}, R_S)-3a**[b]: 4a: **(R_{Fc},R_S)/(S_{Fc},S_S)-4a**

As stated above, no diastereoselectivity was observed under theseoxidation conditions. Other achiral oxidants such as meta-chloroperbenzoic acid[14], *t*BuOOH/$MoO_2(acac)_2$,[15]and also chiral ones such as *t*BuOOH/diethyltartrate/Ti(O*i*Pr)$_4$[16] and *t*BuOOH/diethyltartrate/$MoO_2(acac)_2$ were then employed. Unfortunately, all of them gave lower conversionsand no significant diastereoselectivity improvement relative to Xu's method. Therefore, our investigations werecontinued using the H_2O_2/phenol system. The next step was the oxidation ofenantiomerically pure thiophosphine-thioethers (R_{Fc}) **1a-c 11a, 12**which gave the corresponding thiophosphine-sulfoxides**2a-c** as a mixture of two diastereomers in enantiomerically pure form (Scheme 2).The results obtained working with optically pure thioethersare quite similar to those obtained using the compounds in racemic form. Thus, we have access to the desiredferrocenylthiophosphine-sulfoxidesin diastereoisomerically and enantiomerically pure form.



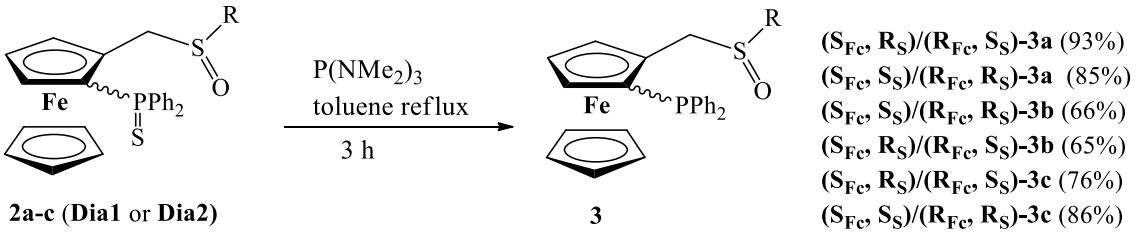
(R_{Fc}) 1a-c

2a-c

2a 87% [(R_{Fc},R_S)+(R_{Fc},S_S)]
2b 87% [(R_{Fc},R_S)+(R_{Fc},S_S)]
2c 90% [(R_{Fc},R_S)+(R_{Fc},S_S)]

Scheme 2

As the thioetheroxidations wereperformed on ferrocene derivatives with thiophosphine group in order to prevent phosphorusoxidation, the next step was the phosphorus deprotectionin order to liberate the free phosphine group and generateferrocenylphosphinesulfoxidesthat can be used as chiral bidentate P-S ligands. This reaction was carried out using tris(dimethylamino)phosphine in refluxing toluene for 3 hours (Scheme 3).[11a] Longer reaction time gave partial deoxygenation of the sulfoxide group. Phosphine-sulfoxide compounds**3a-c**being air sensitive, their purification was accomplishedby column chromatography under argon with yields of isolated products from 65 to 93%. Single crystals of **(S_{Fc}, S_S)/(R_{Fc}, R_S)-3a** were obtained by slow diffusion of pentane vapors into a dichloromethane solution, and the XRD structure is presented in Figure 4.The conformation of this unprotected liganddoesnot show significant differencesrelative tothe protected one **(S_{Fc}, S_S)/(R_{Fc}, R_S)-3a**(Table 1).



Scheme 3

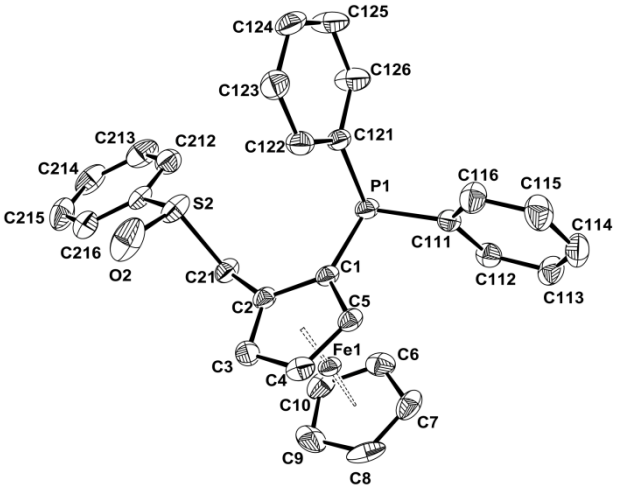


Figure 4.ORTEPview of the phosphine sulfoxyde**3a-Dia2** (S_{Fc}, S_S) with the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for the sake of clarity.

Given that the P,SO ligands could adoptdifferent coordination modes (κ^2-*PS*, κ^2-*PO*, or κ^1-*P*),[17] wecarried out preliminary coordination chemistry investigations with platinum, byreactingthe phosphinesulfoxide ligand **3a** (as the racemic diastereoisomericmixture, Dia1/Dia2 = 1/1) with the platinum precursor $PtCl_2(CH_3CN)_2$. The$^{31}P\{^1H\}$ NMRanalysis of the final mixture shows the presence of two signals corresponding to two similar platinum complexes($\delta1$ = 0.72 ppm, $J_{P\text{-}Pt}$= 3338 Hz and $\delta2$ = 0.47 ppm, $J_{P\text{-}Pt}$ = 3444 Hz) in a 1:1 ratio. The $^1J_{PtP}$value is characteristic of square planar complexes with *cis*chlorine atoms.[18]Crystals of one complex were obtained by diffusion of pentane into a dichloromethane solution, and thus the coordination mode of the sulfoxide group as κ^2-*PS*was determined from the XRD structure (See figure 5).

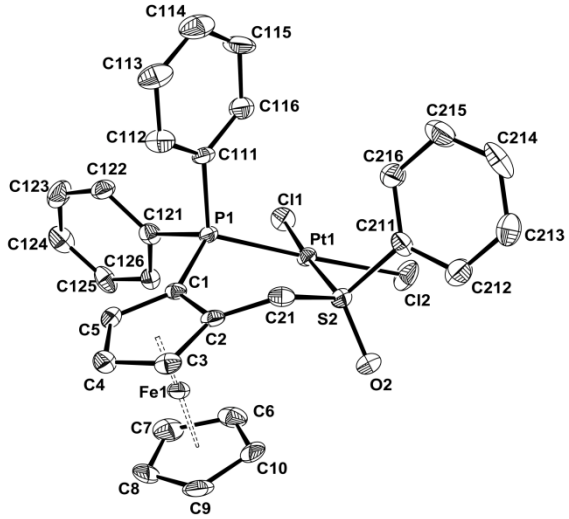
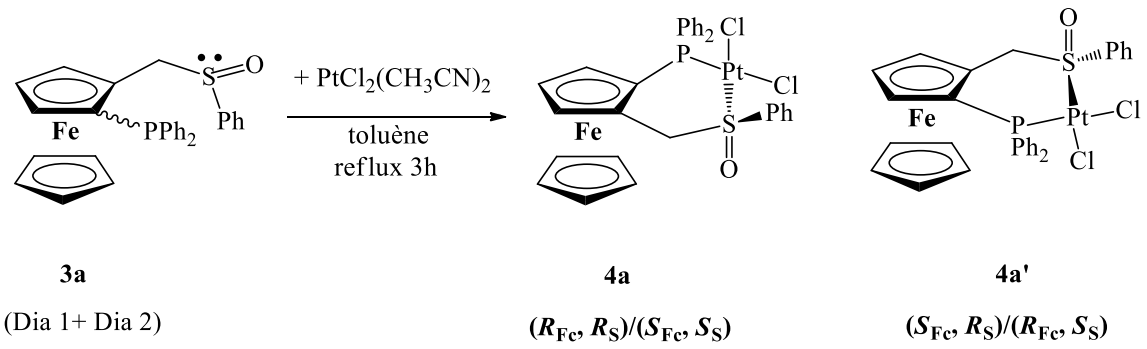


Figure 5.ORTEP view of platinum complex**(R_{Fc},R_S)-4a**with the atom labeling scheme. The other enantiomer (not shown) is also present in the crystal.Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for the sake of clarity.Selected bond lengths (Å): Pt-P: 2,2350(12); Pt-S: 2.2291(12); Pt-Cl1(trans S): 2.2973(12); Pt-Cl2(transP): 2.3312(13); S-O: 1.459.

The Pt atom is surrounded by theS2, P1, Cl1 and Cl2donor atoms in square planar coordination geometry. Itdeviatesfrom the least squares plane defined by these four atoms by only -0.0181(7) Å. The C1, C2, C21, S2, Pt1, P1 metallacycledisplays a boat conformation as indicated by the puckering parameters φ= 302.6(3)° and θ= 87.9(3).[19]The S2 and O2 atoms are *endo* with respect to the Cp1 ring by -0.970(9) Å and -2.186(9) Å respectively. The coordination has induced a slight twist of the two Cp rings (τ = 14.5(4)°) when compared to the uncoordinated ligand which was roughly eclipsed with a twist angle of 4.7(2)°.

The crystallizedcompound corresponds to the racemic diastereomer with the (R_{Fc},R_S)/(S_{Fc},S_S)configuration. Given the similarity of the NMR signals, we attribute to the second compound the structure **4a'** with the (S_{Fc},R_S)/(R_{Fc},S_S) configuration (Scheme 4).



Scheme 4

The presence of two complexes in a 1:1 ratio in the product suggests that the two diastereomericferrocenyl phosphine-sulfoxide ligands do nothave significantly different reactivity with the platinum precursor. This might be surprising given that in the case of the correspondingferrocenyl phosphine thioethers, we observed a total discrimination between the two electron pairs for coordination with platinum, palladium[20] or iridium.[21]Our attempts to obtain complex **4a** by oxidation of the sulfur atom in the coordination sphere of the corresponding phosphine-thioether platinum precursor (Ph_2P-Fc-$CH_2SPh)PtCl_2$[20]were unsuccessful (conditions : mCPBA, THF, reflux, 20h). The oxidation reaction did not occur and the starting material was recovered quantitatively.

3. Conclusion

In conclusion, we have described the synthesis of new ferrocenyl derivatives thiophosphine-sulfoxide**2a-c** and phosphine-sulfoxide**3a-c** having aromatic or aliphatic substituents on the sulfur atom. These ligands possess planar chirality for theferrocenemoiety and central chirality at the sulfur atom and could be obtained as pure diastereoisomersin both racemic andenantiomerically pure form. Most of these compounds were fully characterized by XRD analysis allowingthe absolute configuration assignmentfor each stereoisomer.Preliminarycoordination studies of these ligands were carried out with platinum, demonstrating bidentateκ^2-*PS*complexation in this case. Tests of enantiomerically pure ligands in various catalytic asymmetric reactions are in progress in our laboratories and will be presented in due course.

4. Experimental

4.1 General

All reactions were carried out under argon using standardSchlenkline techniques. Solvents were carefully dried by conventionalmethods and distilled under argon before use. The NMR spectra were recorded on a BrukerDRX-500Avanceinstrument with degased solvents. Elemental analyses were recorded on Perkin Elmer 2400 II. The mass spectrawererecordedon a Nermag R-10-10H spectrometer.

4.2 2-thiodiphenylphosphino-(phenyl-sulfoxymethyl)ferrocene, 2a.

In a Schlenktube under argon were introduced 240 mg (0.45 mmol) of racemic thioether (R/S_{Fc})-**1a** and 500 mg (5.4 mmol) of phenol. The mixture was heated to 35°C, then 0.1 ml of an aqueous solution of H_2O_2 (30%) were slowly added to the reaction medium. The reaction is highly exothermic and within minutes the solution turned black. After 5 minutes,10 ml of ethyl acetate, then 10 ml of a saturated solution of Na_2SO_3, and finally 20 ml of an aqueous solution ofNaOH (10%) were added. The phases were separated and the aqueous phase was

extracted with three portions (10ml) of ethyl acetate. The combined organic layers were washed with water, dried over $MgSO_4$ and then the solvent was removed by evaporation under reduced pressure.Compound **2a**was recovered as an orange solid (yield: 226 mg, 92%). The two diastereomers were separated by chromatography on silica usinga mixture of ether and dichloromethane (1/1) as eluent to give 100 mg of **2a-Dia1, (R_{Fc},S_S)/(S_{Fc},R_S)-2a** (yield: 41%) and 108 mg of **2a-Dia2, (R_{Fc},R_S)/(S_{Fc},S_S)-2a** (yield: 44%).MS (DCI, NH_3):m/z = 541 (M + 1, 20 %); 558(M + NH_4, 100%).

(R_{Fc},S_S)/(S_{Fc},R_S)-2a:^{1}H NMR (δ, 500 MHz, $CDCl_3$):7.86 (2H, m, Ph); 7.65-7.40 (13H, m, Ph); 4.48 (1H, broad s, substCp); 4.44 (5H, s, Cp); 4.35 (1H. broad s, substCp); 4.32 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 4.30 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 3.87 (1H, broad s, substCp).^{13}C{^{1}H} NMR (δ, 125.8 MHz, $CDCl_3$):144.5 (s, quatSPh); 134.8 (d, J_{CP} = 87 Hz, quat PPh_2) ; 133.1 (d, J_{CP} = 86 Hz, quat PPh_2); 132.5 (d, J_{CP} = 11 Hz, PPh_2); 132.3 (d, J_{CP} = 11 Hz, PPh_2); 131.96 (s, PPh_2); 131.9 (s, PPh_2); 131.3 (s, SPh); 129.4 (s, SPh); 128.9 (d, J_{CP} = 13 Hz, PPh_2); 128.6 (d, J_{CP} = 13 Hz, PPh_2); 124.8 (s, SPh); 83.1 (d, J_{CP} = 12 Hz, quatCp); 75.8 (d, J_{CP} = 95Hz, quatCp); 75.4 (d, J_{CP} = 9 Hz, substCp); 74.6 (d, J_{CP} = 12 Hz, substCp); 71.6 (s, Cp); 70.4 (d, J_{CP} = 10 Hz, substCp); 58.0 (s, $\underline{C}H_2$Cp).^{31}P{^{1}H} NMR (δ, 202.5 MHz. $CDCl_3$):43.5. Elemental analysis:$C_{29}H_{25}FePS_2O$; %C (calcd 64.44, found 62.84), % H (calcd 4.63, found 5.03).

(R_{Fc},R_S)/(S_{Fc},S_S)-2a:^{1}H NMR (δ, 500 MHz, $CDCl_3$): 7.89 (2H, m, Ph); 7.87 (2H, m, Ph); 7.6-7.40 (11H, m,Ph); 5.34 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 4.85 (1H, m, substCp); 4.49 (1H, m, substCp); 4.30 (5H, s, Cp); 3.87 (1H, m, substCp); 3.61 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp).^{13}C{^{1}H} NMR (δ, 125.8 MHz, $CDCl_3$): 134.9 (d, J_{CP} = 87 Hz, quat PPh_2); 133.2 (d, J_{CP} = 87 Hz, quat PPh_2); 132.7 (d, J_{CP} = 11 Hz, PPh_2); 132.4 (d, J_{CP} = 11 Hz, PPh_2); 132.1 (d, J_{CP} = 3 Hz, PPh_2); 132.0 (d, J_{CP} = 3 Hz, PPh_2); 130.9 (s, SPh); 129.5 (s, SPh); 129.4 (s, quatSPh); 128.8 (d, J_{CP} = 13 Hz, PPh_2); 128.6 (d, J_{CP} = 13 Hz, PPh_2); 123.9 (s, SPh); 83.0 (d, J_{CP} = 12 Hz, quatCp); 76.2 (d, J_{CP} = 9 Hz, substCp); 75.8 (d, J_{CP} = 12 Hz, substCp); 74.8 (d, J_{CP} = 95Hz, quatCp); 71.4 (s, Cp); 71.1 (d, J_{CP} = 10 Hz, substCp); 61.1 (s, $\underline{C}H_2$Cp). ^{31}P{^{1}H} NMR (δ, 202.5 MHz, $CDCl_3$):43.9; Elemental analysis: $C_{29}H_{25}FePS_2O$; %C (calcd 64.44, found 64.12), % H (calcd 4.63, found 4.32).

4.3 2-thiodiphenylphosphino-(ethyl-sulfoxymethyl)-ferrocene 2b

Following the same procedure described abovefor the synthesis of **2a**, the reaction was realized starting from 250mg (0.52 mmol) of racemic thioether(R/S)$_{Fc}$-**1b**, 500 mg of phenol

and 0.10 ml of an aqueous solution of H_2O_2 (30%). **2b**was recovered as an orange solid (yield: 241 mg, 93%). The two diastereomers were separated by chromatography on silica usinga mixture of ether and dichloromethane (1/1) as eluent to give 114 mg of **2b-Dia1, (*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-2b** (yield: 44%) and 109 mg of **2b-Dia2, (*R*$_{Fc}$,*S*$_S$)/(*S*$_{Fc}$,*R*$_S$)-2b** (yield: 42%).MS (DCI, NH_3):m/z = 493 (M + 1, 45 %); 510 (M + NH_4, 100%).

(*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-2b :^{1}H NMR (δ, 500 MHz. $CDCl_3$): 7.85-7.81 (2H, m, PPh_2); 7.66-7.47 (6H, m, PPh_2); 7.43 (2H, broad s, PPh_2); 4.90 (1H, s, subst Cp); 4.47 (1H, s, subst Cp); 4.36 (5H, s, Cp); 4.45-4.28 (2H, m, C$\underline{H}_2$Cp); 3.87 (1H, s, subst Cp); 2.35 (2H, broad s, C$\underline{H}_2$CH$_3$); 1.1 (3H, broad s, CH$_2$C$\underline{H}_3$). ^{13}C{^{1}H} NMR (δ, 125.8 MHz. $CDCl_3$): 133.9 (d, J_{CP} = 87 Hz, quat PPh_2); 132.1 (d, J_{CP} = 86 Hz, quat PPh_2); 132.0 (d, J_{CP} = 11 Hz, PPh_2); 131.9 (s, PPh_2); 131.8 (broad s, PPh_2); 128.7 (d, J_{CP} = 12 Hz, PPh_2); 128.5 (d, J_{CP} = 12 Hz, PPh_2); 82.0 (d, J_{CP} = 12 Hz, quat Cp); 74.8 (s, subst Cp); 74.7 (d, J_{CP} = 12 Hz, subst Cp); 74.0 (d, J_{CP} = 96 Hz, quat Cp); 71.3 (s, Cp); 70.8 (d, J_{CP} = 10 Hz, subst Cp); 50.6 (s, $\underline{C}$H$_2$Cp); 44.7 (s, $\underline{C}$H$_2$CH$_3$); 7.6 (s, CH$_2\underline{C}$H$_3$). ^{31}P{^{1}H} NMR (δ, 202.5 MHz, $CDCl_3$): 41.06. Elemental analysis:$C_{25}H_{25}FePS_2O$; %C (calcd 60.98, found 61.08), % H (calcd 5.08, found 5.17).

(*R*$_{Fc}$,*S*$_S$)/(*S*$_{Fc}$,*R*$_S$)-2b: ^{1}H NMR (δ, 500 MHz. $CDCl_3$): 7.83-7.79 (2H, m,PPh_2); 7.59-7.48 (6H, m, PPh_2); 7.41 (2H, broad s, PPh_2); 5.26 (1H, d(AB),J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 4.81 (1H, s, subst Cp); 4.47 (1H, s, subst Cp); 4.32 (5H, s, Cp); 3.82 (1H, s, subst Cp); 3.53 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 2.65 (2H, q, J_{HH} = 7 Hz, C$\underline{H}_2$CH$_3$); 1.5 (3H, broad s, CH$_2$C$\underline{H}_3$). ^{13}C{^{1}H} NMR (δ, 125.8 MHz, $CDCl_3$):134.1 (d, J_{CP} = 88 Hz, quat PPh_2); 132.3 (d, J_{CP} = 88 Hz, quat PPh_2); 132.0 (d, J_{CP} = 11 Hz, PPh_2); 131.9 (broad s, PPh_2); 128.6 (d, J_{CP} = 12 Hz, PPh_2); 128.5 (d, J_{CP} = 13 Hz, PPh_2); 82.5 (d, J_{CP} = 10 Hz, quat Cp); 75.8 (d, J_{CP} = 9 Hz, subst Cp); 75.5 (d, J_{CP} = 12 Hz, subst Cp); 73.1 (d, J_{CP} = 95Hz,quat Cp); 71.2 (s, Cp); 71.1 (s, subst Cp); 53.4 (s, $\underline{C}$H$_2$Cp); 46.7 (s, $\underline{C}$H$_2$CH$_3$); 7.1 (s, CH$_2\underline{C}$H$_3$). ^{31}P{^{1}H} NMR (δ, 202.5 MHz, $CDCl_3$):41.6.Elemental analysis: $C_{25}H_{25}FePS_2O$; %C (calcd 60.98, found 60.98), % H (calcd 5.08, found 4.83).

4.4 2-thiodiphenylphosphino-(*tert*-butyl-sulfoxymethyl)-ferrocene2c

Following the same procedure described abovefor the synthesis of **2a**, the reaction was carried outstarting from 250mg (0.496 mmol) of racemic thioether(*R*/*S*)$_{Fc}$-**1c**, 500 mg of phenol and 0.10 ml of an aqueous solution of H_2O_2 (30%). **2c**was recovered as an orange solid (yield: 237 mg, 92%). The two diastereomers were separated by chromatography on silica usinga mixture of ether and acetone (5%) as eluent to give 111 mg of **2c-Dia1, (*R*$_{Fc}$,*S*$_S$)/(*S*$_{Fc}$,*R*$_S$)-2c** (yield:

43%) and 103 mg of **2c-Dia2, (*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-2c** (yield: 40%).MS (DCI, NH_3): m / z = 521 (M + 1, 100 %); 538 (M + NH_4, 80%).

(*R*$_{Fc}$,*S*$_S$)/(*S*$_{Fc}$,*R*$_S$)-2c: ^{1}H NMR (δ,500 MHz, $CDCl_3$):7.8 (2H, m, PPh_2); 7.58-7.47 (6H, m, PPh_2); 7.40 (2H, m, PPh_2); 5.07 (1H, broad s, subst Cp); 4.47 (1H, broad s, C$\underline{H}_2$Cp); 4.41(5H, s, Cp) ; 4.41(1H, s, subst Cp); 3.78 (1H, s, subst Cp); 3.05 (1H, d(AB), J_{HH} = 14 Hz, C$\underline{H}_2$Cp); 1.32 (9H, s, C(C$\underline{H}_3$)$_3$). ^{13}C{^{1}H} NMR (δ,125.8 MHz, $CDCl_3$): 134.6 (d, J_{CP} = 87 Hz, quat PPh_2); 132.4 (d, J_{CP} = 86 Hz, quat PPh_2); 131.9 (d, J_{CP} = 11 Hz, PPh_2); 131.7 (d, J_{CP} = 11 Hz, PPh_2); 131.6 (d, J_{CP} = 3 Hz, PPh_2); 131.5 (d, J_{CP} = 3 Hz, PPh_2); 128.6 (d, J_{CP} = 13 Hz, PPh_2); 128.2 (d, J_{CP} = 13 Hz, PPh_2); 85.2 (d, J_{CP} = 12 Hz, quat Cp); 74.9 (d, J_{CP} = 96 Hz, quat Cp); 73.8 (d, J_{CP} = 12 Hz, subst Cp); 73.6 (d, J_{CP} = 19 Hz, subst Cp); 71.1 (s, Cp); 70.0 (d, J_{CP} = 9 Hz, subst Cp); 54.2 (broad s, $\underline{C}$(CH$_3$)$_3$); 44.9 (s, $\underline{C}$H$_2$Cp); 23.1 (s, C($\underline{C}$H$_3$)$_3$). ^{31}P{^{1}H} NMR (δ,202.5 MHz, $CDCl_3$): 41.8. Elemental analysis: $C_{27}H_{29}FePS_2O$; %C (calcd 62.31, found 62.16), % H (calcd 5.58, found 5.54).

(*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-2c: ^{1}H NMR (δ,500 MHz, $CDCl_3$): 7.83 (1H, dd, J_{HH} = 2 Hz, J_{HP} = 14 Hz, m C$_6\underline{H}_5$); 7.82 (1H, dd,J_{HH} = 2 Hz, J_{HP} = 15Hz, m C$_6\underline{H}_5$); 7.66 (1H, dd, J_{HH} = 2 Hz, J_{HP} = 15Hz, m C$_6\underline{H}_5$); 7.65 (1H, dd, J_{HH} = 2 Hz, J_{HP} = 15Hz, m C$_6\underline{H}_5$); 7.58-7.53 (1H, m, p C$_6\underline{H}_5$); 7.52-7.45 (3H, m, p+2o C$_6\underline{H}_5$); 7.42-7.37 (2H, m, 2o C$_6\underline{H}_5$); 5.09 (1H, d(AB). J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 4.89 (1H, m, subst Cp); 4.43 (1H, m, subst Cp); 4.37 (5H, s, Cp); 3.75 (1H, m, subst Cp); 3.28 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 1.04 (9H, s,C(C$\underline{H}_3$)$_3$). ^{13}C{^{1}H} NMR (δ,125.8 MHz. $CDCl_3$):134.02 (d, J_{CP} = 87 Hz, quat PPh_2); 132.87 (d, J_{CP} = 82 Hz, quat PPh_2); 132.53 (d, J_{CP} = 10 Hz, m PPh_2); 131.97 (d, J_{CP} = 10 Hz, m PPh_2); 131.50 (d, J_{CP} = 3 Hz, pPPh_2); 131.45 (d, J_{CP} = 3 Hz, p PPh_2); 128.23 (d, J_{CP} = 4 Hz, o PPh_2); 128.13 (d. J_{CP} = 4 Hz, o PPh_2); 83.50 (d, J_{CP} = 12 Hz, quat Cp); 75.20 (d, J_{CP} = 9 Hz, subst Cp); 75.07 (d, J_{CP} = 13 Hz, subst Cp); 74.47 (d, J_{CP} = 95Hz, quat Cp); 71.04 (s, Cp); 70.41 (d, J_{CP} = 10 Hz, subst Cp); 53.23 (s, $\underline{C}$(CH$_3$)$_3$); 47.84 (s, $\underline{C}$H$_2$Cp); 22.75 (s, C($\underline{C}$H$_3$)$_3$). ^{31}P{^{1}H} NMR (δ,202.5 MHz. $CDCl_3$):41.4.Elemental analysis:$C_{27}H_{27}FePS_2O$; %C (calcd 62.31, found 59.81), % H (calcd 5.58, found 5.58).

4.5 Synthesis of enantiomerically pure (*R*$_{Fc}$) 2-thiodiphenylphosphino-(phenylsulfoxymethyl) ferrocene,(*R*$_{Fc}$)-2a.

The reaction was carried out using enantiomericallypure **(*R*$_{Fc}$)-1a**following the same procedure described above for the synthesis of racemic **2a. Dia1, (*R*$_{Fc}$,*S*$_S$)-2a** : $[\alpha]_D$ = -100.2; ($CHCl_3$. c=0.49); **Dia2, (*R*$_{Fc}$,*R*$_S$)-2a** : $[\alpha]_D$ = +14.2; ($CHCl_3$. c=0.49).

4.6 (R_{Fc}) 2-thiodiphenylphosphino-(ethylsulfoxymethyl) ferrocene,(R_{Fc})-2b.

The reaction was carried out using enantiomericallypure **(R_{Fc})-1b**following the same procedure described above for the synthesis of racemic **2b.Dia1, (R_{Fc},R_S)-2b**: $[\alpha]_D$ = -110.2; ($CHCl_3$. c=0.5); **Dia2,(R_{Fc},S_S)-2b**: $[\alpha]_D$ = +32.1; ($CHCl_3$. c=0.505).

4.7 (R_{Fc}) 2-thiodiphenylphosphino-(*tert*-butylsulfoxymethyl) ferrocene,(R_{Fc})-2c.

The reaction was carried out using enantiomerically pure **(R_{Fc})-1c**following the same procedure described above for the synthesis of racemic **2c.Dia1, (R_{Fc},S_S)-2c**: $[\alpha]_D$ = -152.2; ($CHCl_3$. c=0.5); **Dia2,(R_{Fc},R_S)-2c**: $[\alpha]_D$ = +5.0; ($CHCl_3$. c=0.515).

4.8 (R_{Fc},S_S)/(S_{Fc},R_S)-2-diphenylphosphino-(phenyl-sulfoxymethyl)-ferrocene,3a-Dia1.

In a Schlenktube under argon were introduced 81 mg (0.15 mmol) of racemic sulfoxide**(R_{Fc}, S_S)/(S_{Fc},R_S)-2a-Dia1** in 5 ml of toluene and 0.2 ml (0.18 g, 1.1 mmol) of tris(dimethylamino)phosphine. After reflux for 3 h, the solvent wasremoved by evaporation and the crude sulfoxide phosphine **(R_{Fc},S_S)/(S_{Fc},R_S)-3a-Dia1** was obtained as an orange liquid (yield: 71mg, 93%). ^{1}H NMR (δ,500 MHz. $CDCl_3$): 7.64-7.49 (4H, m, Ph); 7.49-7.32 (6H, m, Ph); 7.32-7.12 (5H, m, Ph); 4.43 (1H, dd(ABX), J_{HH} = 13 Hz, J_{HP} = 2 Hz, C$\underline{H}_2$Cp); 4.42 (1H, broad s, substCp); 4.22 (1H, t, J_{HH} = 2 Hz, substCp); 4.01 (5H, s, Cp); 3.90 (1H, broad s, substCp); 3.74 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp). ^{31}P{^{1}H} NMR (δ, 202.5 MHz, $CDCl_3$):-22.5.

4.9 (R_{Fc},R_S)/(S_{Fc},S_S)-2-diphenylphosphino-(phenyl-sulfoxymethyl)-ferrocene,3a-Dia2.

Following the same procedure described abovefor the desulfurisation of **(R_{Fc},S_S)/(S_{Fc},R_S)-2a-Dia1**, the reaction was realized from 92mg (0.17 mmol) of racemic sulfoxide**(R_{Fc},R_S)/(S_{Fc},S_S)-2a-Dia2** and 0.2 ml (0.18 g, 1.1 mmol) of tris(dimethylamino)phosphine. The sulfoxide phosphine product **(R_{Fc},R_S)/(S_{Fc},S_S)-3a-Dia2**wasobtained as an orange solid (yield:73 mg,85%). ^{1}H NMR (δ,500 MHz, $CDCl_3$):7.65-7.5 (3H, m, Ph); 7.5-7.35 (6H, m, Ph); 7.35-7.2 (6H, m, Ph); 4.77 (1H, d, J_{HH} = 1 Hz, substCp); 4.43 (1H, t, J_{HH} = 3 Hz, substCp); 4.17 (1H, dd(ABX), J_{HH} = 13 Hz, J_{HP} = 3 Hz, C$\underline{H}_2$Cp); 3.99 (5H, s, Cp); 3.85 (1H, t, J_{HH} = 1 Hz, substCp); 3.77 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp). ^{31}P{^{1}H} NMR (δ, 202.5 MHz, $CDCl_3$):-20.9.

4.10 (R_{Fc},R_S)/(S_{Fc},S_S)-2-diphenylphosphino-(ethylsulfoxymethyl) ferrocene,3b-Dia1.

In a Schlenktube under argon were introduced 77 mg (0.157mmol) of the racemic sulfoxide**(R_{Fc},R_S)/(S_{Fc},S_S)-2b-Dia1** in 5 ml of toluene and 0.2 ml (0.18 g, 1.1 mmol) of tris(dimethylamino)phosphine. After reflux for 2 h, the solvent was evaporatedunder reduced pressure and the crude reaction productwas purified by column chromatography on silica usingdegased ether/dichloromethane mixture (1/0 - 1/1) as eluent. The sulfoxide phosphine product **(R_{Fc},R_S)/(S_{Fc},S_S)-3b-Dia1** was obtained as an orange solid (yield:48mg, 66%).^{1}H NMR (δ,500 MHz, $CDCl_3$):7.62-7.50 (3H, m, Ph); 7.44-7.35 (2H, m, Ph); 7.28-7.08 (5H, m, Ph); 4.62 (1H, q, J_{HH} = 1 Hz, substCp); 4.39 (1H, t, J_{HH} = 3 Hz, substCp); 4.15 (1H, dd(ABX), J_{HH} = 14 Hz, J_{HP} = 2 Hz, C$\underline{H}_2$Cp); 4.03 (5H, s, Cp); 3.93 (1H, d, J_{HH} = 1 Hz substCp); 3.76 (1H, d(AB), J_{HH} = 14 Hz, C$\underline{H}_2$Cp); 2.37 (1H, dq, J_{HH} = 7.7 Hz, J_{HP} = 2.7 Hz, C$\underline{H}_2$CH$_3$); 1.12 (1H, t, J_{HH} = 7.7 Hz, CH$_2$C$\underline{H}_3$). ^{31}P{^{1}H} NMR (δ,202.5 MHz, $CDCl_3$):-22.5.MS (DCI, NH_3):m/z = 461(M + 1, 100 %).

4.11 (R_{Fc},S_S)/(S_{Fc},R_S)-2-diphenylphosphino-(ethylsulfoxymethyl) ferrocene,3b-Dia2.

Following the same procedure described abovefor the desulfurisation of **(R_{Fc},R_S)/(S_{Fc},S_S)-2b-Dia1**, the reaction was realized from 55mg (0.112 mmol) of racemic sulfoxide**(R_{Fc},S_S)/(S_{Fc},R_S)-2b-Dia2** and 0.2 ml (0.18 g, 1.1 mmol) of tris(dimethylamino)phosphine. The crudereaction product waspurified by column chromatography on silica usingdegased ether/methanol mixture (1/0 – 95/5) as eluent. The sulfoxide phosphine product **(R_{Fc},S_S)/(S_{Fc},R_S)-3b-Dia2**wasobtained as an orange solid (yield: 33 mg, 65%). ^{1}H NMR (δ,500 MHz, $CDCl_3$):7.62-7.48 (3H, m, Ph); 7.43-7.35 (3H, m, Ph); 7.30-7.13 (4H, m, Ph); 4.72 (1H, d, J_{HH} = 1.5Hz, substCp); 4.41 (1H, t, J_{HH} = 1 Hz, substCp); 4.10 (1H, dd(ABX), J_{HH} = 13 Hz, J_{HP} = 3 Hz, C$\underline{H}_2$Cp); 4.01 (5H, s, Cp); 3.87 (1H, t, J_{HH} = 1 Hz, substCp); 3.72 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 2.45 (1H, dq, J_{HH} = 7.6 Hz, J_{HP} = 3 Hz, C$\underline{H}_2$CH$_3$); 1.10 (1H, t, J_{HH} = 7.6 Hz, CH$_2$C$\underline{H}_3$). ^{31}P{^{1}H} NMR (δ,202.8 MHz, $CDCl_3$):-21.5.

4.12 (R_{Fc},S_S)/(S_{Fc},R_S)-2-diphenylphosphino-(*tert*-butylsulfoxymethyl) ferrocene,3c-Dia1.

In a Schlenktube under argon wereintroduced 50 mg (0.096mmol) of the sulfoxidecompound **(R_{Fc},S_S)/(S_{Fc},R_S)-2c-Dia1** in 5 ml of toluene and 0.1 ml (90 g, 0.55 mmol) of tris(dimethylamino)phosphine. After reflux for 2 h, the solvent wasremoved and the crudereaction product waspurified by column chromatography on silica usingdegased ether/dichloromethane mixture (1/1) as eluent. the sulfoxide phosphine product **(R_{Fc},S_S)/(S_{Fc},R_S)-3c-Dia1**wasobtained as an orange liquid (yield: 36mg, 76%).^{1}H NMR (δ,500 MHz, $CDCl_3$) :7.58-7.42 (2H, m, Ph); 7.43-7.32 (3H, m, Ph); 7.30-7.18 (3H, m, Ph);

7.18-7.05 (2H, m, Ph); 4.79 (1H, s broad, substCp); 4.34 (1H, t, J_{HH} = 1 Hz, substCp); 4.08 (5H,s,Cp); 3.82 (1H,t, J_{HH} = 1 Hz, substCp); 3.73 (1H, dd(ABX), J_{HH} = 12 Hz, J_{HP} = 2 Hz, C$\underline{H}_2$Cp); 3.30 (1H, d(AB), J_{HH} = 12 Hz, C$\underline{H}_2$Cp); 1.2 (9H, s, C(C$\underline{H}_3$)$_3$). $^{31}P\{^1H\}$ NMR (δ,202.8 MHz, $CDCl_3$):-20.6.

4.13 (*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-2-diphenylphosphino-(*tert*-butylsulfoxymethyl) ferrocene, 3c-Dia2.

Following the same procedure described abovefor the desulfurisation of **(*R*$_{Fc}$,*S*$_S$)/(*S*$_{Fc}$,*R*$_S$)-2c-Dia1**, the reaction was realized from 70mg (0.135 mmol) of the sulfoxide compound**(*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-2c-Dia2** and 0.2 ml (0.18 g, 1.1 mmol) of tris(dimethylamino)phosphine. The sulfoxide phosphine product **(*R*$_{Fc}$,*R*$_S$)/(*S*$_{Fc}$,*S*$_S$)-3c-Dia2** wasobtained as an orange solid (yield: 57 mg, 86%). ^1H NMR (δ,500 MHz, $CDCl_3$):7.57-7.46 (3H, m, Ph); 7.42-7.34 (2H, m, Ph); 7.28-7.12 (5H, m, Ph); 4.78 (1H, d, J_{HH} = 2 Hz, substCp); 4.38 (1H, t, J_{HH} = 1 Hz, substCp); 4.06 (1H, dd(ABX), J_{HH} = 13 Hz, J_{HP} = 2 Hz, C$\underline{H}_2$Cp); 4.04 (5H, s, Cp); 3.75 (1H, d, J_{HH} = 1 Hz, substCp); 3.36 (1H, d(AB), J_{HH} = 13 Hz, C$\underline{H}_2$Cp); 1.05 (9H, s, C(C$\underline{H}_3$)$_3$). $^{31}P\{^1H\}$ NMR (δ,202.8 MHz, $CDCl_3$):-20.9.

X-ray analyses

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD diffractometer for **2a-Dia1**, **2a-Dia2**, **2b-Dia1** and**3a-Dia2**ora Stoe IPDS diffractometer for **2c-Dia1**, **2c-Dia2** and **4a**. Data were collected using the monochromatic MoKα radiation (λ= 0.71073).

The structures were solved by direct methods (SIR97[21]) and refined by least-squares procedures on F^2 using SHELXL-97.[22] All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The drawing of the molecules was realised with the help of ORTEP32.[24] Crystal data and refinement parameters are shown in Table 2.

Table 2.Crystal data and structure refinement parameters.

Identification code	**2a-Dia1**	**2a-Dia2**	**2b-Dia1**
Empirical formula	$C_{29}H_{25}FeOPS_2$	$C_{29}H_{25}FeOPS_2$	$C_{25}H_{25}FeOPS_2$
Formula weight	540.43	540.43	492.39
Temperature, K	180(2)	180(2)	180(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	Cc	P 2_1/a	Pcab
a, Å	14.5928(10)	12.812(2)	8.1197(6)
b, Å	18.4079(11)	9.4172(16)	16.9489(11)
c, Å	9.4244(6)	21.896(4)	33.823(2)
α, °	90.0	90.0	90.0
β, °	93.858(5)	104.832(16)	90.0
γ, °	90.0	90.0	90.0
Volume, $Å^3$	2525.9(3)	2553.8(8)	4654.7(5)
Z	4	4	8
Density (calcd), Mg/m^3	1.421	1.322	1.405
Absorption coefficient, mm^{-1}	0.847	0.754	0.911
F(000)	1120	1056	2048
Crystal size, mm^3	0.45x0.42x0.2	0.16 x 0.10 x 0.05	0.52x 0.39 x 0.12
Theta range, °	3.56 to 27.81	2.71 to 26.03	3.32 to 26.37
Reflections collected	9974	18130	33297
Independent reflections [R(int)]	4487 (0.0242)	5055 (0.1527)	4751 (0.0634)
Completeness, %,	99.7	99.7	99.8
Absorption correction	Multiscan	Multi-scan	Multi-scan
Max. , min. transmission	0.8415 and 0.6881	1.0500 and 0.8078	0.8230 and 0.6750
Refinement method	F^2	F^2	F^2
Data / restraints / parameters	4487 / 2 / 308	5055 / 0 / 307	4751 / 0 / 272
Goodness-of-fit on F^2	1.055	0.892	1.081
Final R indices [I>2sigma(I)]	0.0278, 0.0642	0.0662, 0.1564	0.0514, 0.1035
R indices (all data)	0.0305, 0.0656	0.1713, 0.2309	0.0704, 0.1118
Absolute structure parameter	0.019(14)		
Largest diff. peak and hole, $e.Å^{-3}$	0.326 and -0.219	0.711 and -0.865	0.417 and -0.367

Table 1. Crystal data and structure refinement(Contd.).

Identification code	**2c-Dia1**	**2c-Dia2**	**3a-Dia2**
Empirical formula	$C_{27}H_{29}FeOPS_2$	$C_{27}H_{29}FeOPS_2$	$C_{29}H_{25}FeOPS$
Formula weight	520.44	520.44	508.37
Temperature, K	180(2)	180(2)	180(2)
Wavelength, Å	0.71073	0.71073	0.70930
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	Cc	$P2_1$	P -1
a, Å	11.8130(12)	14.7673(14)	7.8035(8)
b, Å	14.8503(12)	10.1912(7)	9.3075(9)
c, Å	13.9653(16)	17.0533(18)	17.5040(15)
α, °	90.0	90.0	79.331(7)
β, °	91.394(13)	98.030(12)	87.727(7)
γ, °	90.0	90.0	77.299(8)
Volume, $Å^3$	2449.2(4)	2541.3(4)	1218.8(2)
Z	4	4	2
Density (calcd), Mg/m^3	1.411	1.360	1.385
Absorption coefficient, mm^{-1}	0.870	0.838	0.790
F(000)	1088	1088	528
Crystal size, mm^3	0.76 x 0.22 x 0.2	0.56 x 0.52 x 0.02	0.35 x 0.32 x 0.2
Theta range, °	2.62 to 26.04	2.33 to 26.08	3.47 to 28.22
Reflections collected	11892	21668	10784
Independent reflections [R(int)]	4769 (0.0442)	9539 (0.0730)	6009 (0.0237)
Completeness, %,	98.8	97.7	99.1
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. , min. transmission	0.943 and 0.610	0.8058 and 0.7391	0.7521 and 0.6862
Refinement method	F^2	F^2	F^2
Data / restraints / parameters	4769 / 2 / 292	9539 / 1 / 584	6009 / 0 / 298
Goodness-of-fit on F^2	1.025	0.843	0.991
Final R indices [I>2sigma(I)]	0.0302, 0.0778	0.0379, 0.0611	0.0389, 0.1012
R indices (all data)	0.0314, 0.0785	0.0716, 0.0685	0.0507, 0.1067
Absolute structure parameter	-0.004(11)	0.284(14)	
Largest diff. peak and hole, $e.Å^{-3}$	0.318 and -0.384	0.328 and -0.425	1.418 and -0.385

Table 1.Crystal data and structure refinement(Contd.).

Identification code	**4a**
Empirical formula	$C_{29}H_{25}Cl_2FeOPPt\ S$
Formula weight	774.36
Temperature, K	180(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	18.6057(14)
b, Å	7.5780(7)
c, Å	19.3027(14)
α, °	90.0
β, °	107.659(8)
γ, °	90.0
Volume, $Å^3$	2593.3(4)
Z	4
Density (calcd), Mg/m^3	1.983
Absorption coefficient, mm^{-1}	6.319
F(000)	1504
Crystal size, mm^3	0.18 x 0.08 x 0.08
Theta range, °	2.21 to 26.06
Reflections collected	24800
Independent reflections [R(int)]	5081 (0.0562)
Completeness, %,	99.0
Absorption correction	Multi-scan
Max. , min. transmission	0.5281 and 0.4506
Refinement method	F^2
Data / restraints / parameters	5081 / 0 / 325
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	0.0289, 0.0585
R indices (all data)	0.0445, 0.0624
Absolute structure parameter	
Largest diff. peak and hole, $e.Å^{-3}$	0.907 and -0.927

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